PATENT ABSTRACTS OF JAPAN

(11)Publication number : 2002-155143
(43)Date of publication of application : 28.05.2002

10L (6)

(51)Int.Cl. C08G 77/22
C09D183/05
C09D185/04

(21)Application number : 2001-068771
(22)Date of filing : 12.03.2001

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(30)Priority
Priority number : 2000272093 Priority date : 07.09.2000 Priority country : JP

(54) BORAZINE-CONTAINING SILICONE POLYMER AND METHOD FOR PREPARING THIN FILM THEREOF

(57)Abstract:
PROBLEM TO BE SOLVED: To provide an efficient method for preparing a thin film of a borazine- containing silicone polymer that is useful as a coating film or the like with combustion resistance and heat resistance, and a novel borazine-containing silicone polymer.
SOLUTION: A B,B',B″-trialkynyl borazine compound is mixed with a silicon compound having at least two hydrosilyl groups in the presence of a platinum catalyst to form a solution. The solution is applied to the surface of a material to form a thin film of this polymer.

LEGAL STATUS

[Date of request for examination]	12.03.2001
[Date of sending the examiner's decision of rejection]	
[Kind of final disposal of application other than the examiner's decision of rejection or application converted registration]	
[Date of final disposal for application]	
[Patent number]	3459985
[Date of registration]	15.08.2003
[Number of appeal against examiner's decision of rejection]	
[Date of requesting appeal against examiner's decision of rejection]	
[Date of extinction of right]	

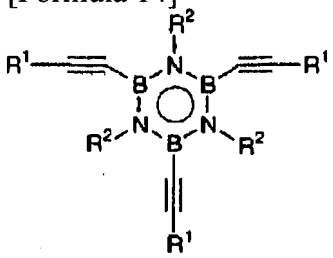
* NOTICES *

1.This document has been translated by computer. So the translation may not reflect the original precisely.
2.**** shows the word which can not be translated.
3.In the drawings, any words are not translated.

DETAILED DESCRIPTION

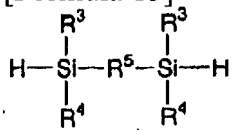
[Detailed Description of the Invention]
[0001]
[The field for techniques to which invention belongs] This invention relates to the manufacture approach of the thin film of a borazine content silicon system polymer useful as coating film, such as flammability-proof and thermal resistance, and a new borazine content silicon system polymer.
[0002]
[Description of the Prior Art] Although the borazine content silicon system polymer showed the thermal stability which was excellent also in air and the application to flammability-proof, a heat-resistant coating ingredient, etc. was expected, the simple example of manufacture of a thin film was not known yet. Moreover, the borazine content silicon system polymer which has the available shape of a straight chain and annular polysiloxane structure industrially was not manufactured. Furthermore, the borazine content silicon system copolymerization polymer of the 3 yuan system which can stop the amount of the borazine monomer used was not known including a usual gene or the usual Tori Inn compound as a monomer component, either.
[0003]
[Problem(s) to be Solved by the Invention] This invention aims at offering the borazine content silicon system polymer which has an efficient manufacturing method, and the new shape of a straight chain and the annular polysiloxane structure of the thin film excellent in the flammability-proof of a borazine content silicon system polymer, and thermal resistance. Moreover, this invention aims at offering the efficient manufacture approach of a thin film excellent in the flammability-proof of the borazine content silicon system copolymerization polymer of the new 3 yuan system which can stop the amount of the borazine monomer used including a usual gene or the usual Tori Inn compound as a monomer component, and this copolymerization polymer, and thermal resistance.
[0004]
[Means for Solving the Problem] As a result of repeating research wholeheartedly that said technical problem should be solved, this invention persons B, B', and B"-thoria RUKINIRU borazines By mixing the silicon compound which has two or more hydrosilyl radicals under existence of a platinum content catalyst, and applying the solution While finding out the new fact that the thin film of the borazine content silicon system polymer generated by the addition reaction of the hydrosilyl radical to an alkynyl group was obtained easily, the new borazine content silicon system polymer which has the shape of a straight chain and annular polysiloxane structure was found out. Moreover, this invention persons found out the new fact that the thin film of a new 3 yuan system borazine content silicon system copolymerization polymer was obtained easily, by the addition reaction of the hydrosilyl radical to an alkynyl group by mixing under B, B', and existence of the silicon compound which has two or more hydrosilyl radicals combining B"-thoria RUKINIRU borazines, and a gene or the Tori Inn compound, and a platinum content catalyst, and applying the solution.
[0005] That is, this invention takes the following configurations.
1. General formula (1)

[0006]
[Formula 14]



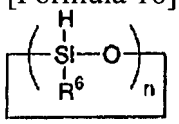
(1)

[0007] (-- a formula -- inside -- R -- one -- an alkyl group -- an aryl group -- an aralkyl -- a radical -- or -- a hydrogen atom -- being shown -- R -- two -- an alkyl group -- an aryl group -- an aralkyl -- a radical -- or -- a hydrogen atom -- being shown --) -- expressing -- having -- B -- B -- ' -- B -- " - a thoria -- RUKINIRU -- borazine -- a compound -- at least -- two -- a piece -- more than -- hydrosilyl -- a radical -- having -- silicon -- a compound -- a platinum catalyst -- existence -- the bottom -- mixing -- the -- a solution -- applying -- things -- the description -- ** -- carrying out -- borazine -- content -- silicon -- a system -- a polymer -- a thin film -- manufacture -- an approach .
The silicon compound which has 2.2 or more hydrosilyl radicals is a general formula (2).
[0008]
[Formula 15]



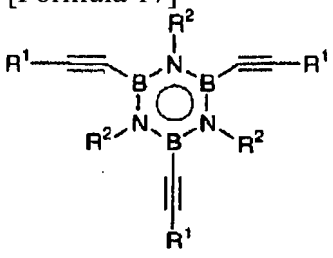
(2)

[0009] It is the manufacture approach given in 1 characterized by being the bis(hydrosilane) compound expressed with (R3 and R4 show among a formula the same or divalent radical of the aromatic series in which the univalent radical which is different from each other may be shown, and R5 may have the substituent by which it is chosen from an alkyl group, an aryl group, an aralkyl radical, or a hydrogen atom, an oxygen atom, or an oxy-poly (dimethyl siloxy) radical).
The silicon compound which has 3.2 or more hydrosilyl radicals is a general formula (3).
[0010]
[Formula 16]



(3)

[0011] It is the manufacture approach given in 1 characterized by being the Pori (hydrosilane) compound expressed with (R6 shows an alkyl group, an aryl group, or an aralkyl radical among a formula, and n shows three or more integers).
4. General formula (1)
[Formula 17]



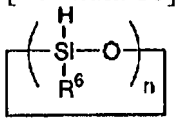
(1)

[0012] (-- a formula -- inside -- R -- one -- an alkyl group -- an aryl group -- an aralkyl -- a radical -- or -

- a hydrogen atom -- being shown -- R -- two -- an alkyl group -- an aryl group -- an aralkyl -- a radical -- or -- a hydrogen atom -- being shown --) -- expressing -- having -- B -- B -- ' -- B -- " - a thoria -- RUKINIRU -- borazine -- a compound -- a general formula (3) --

[0013]

[Formula 18]

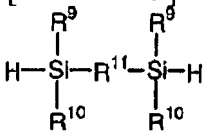


(3)

[0014] (R6 shows an alkyl group, an aryl group, or an aralkyl radical among a formula, and n shows three or more integers) Or a general formula (4)

[0015]

[Formula 19]



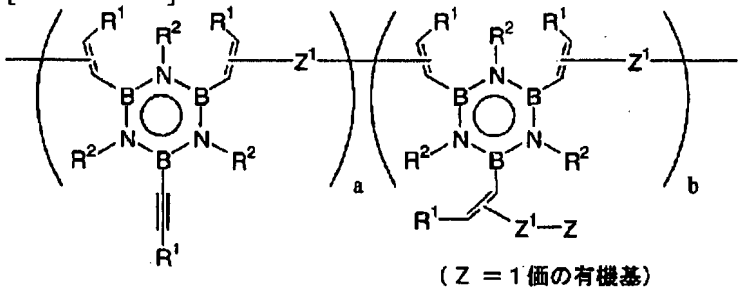
(4)

[0016] (-- R9 and R10 are chosen from an alkyl group, an aryl group, an aralkyl radical, or a hydrogen atom among a formula -- the same -- or -- difference -- a univalent radical is shown and R11 shows an oxy-poly (dimethyl siloxy) radical --) -- the borazine content silicon system polymer which the silicon compound which has at least two or more hydrosilyl radicals expressed is made to react, and is obtained.

5. General formula (5)

[0017]

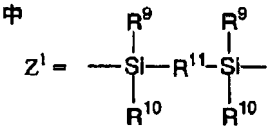
[Formula 20]



(5)

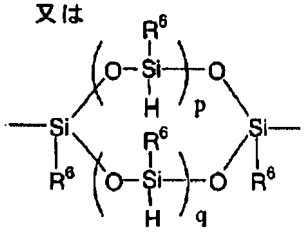
（Z ＝1価の有機基）

式中



（化合物（4）との反応の場合）

又は



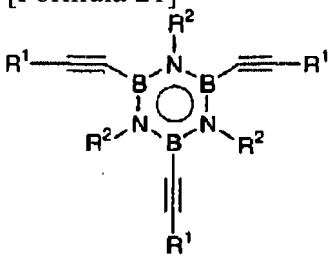
（化合物（3）との反応の場合）

(p＋q＋2＝n)

を示す。

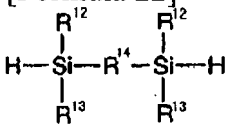
[0018] (-- R1, R2, R9, R10, R11, and R6 are the same as the thing in said general formula (1), (3), and (4) among a formula, and a and b are a+b>=1 for zero or more integers --) -- a borazine content silicon

system polymer given in 4 characterized by having the structure expressed.
6. 4 characterized by whenever [in the inside of air / 5% weight temperature decrease] being 200 degrees C or more, or borazine content silicon system polymer given in 5.
7. General formula (1)
[0019]
[Formula 21]



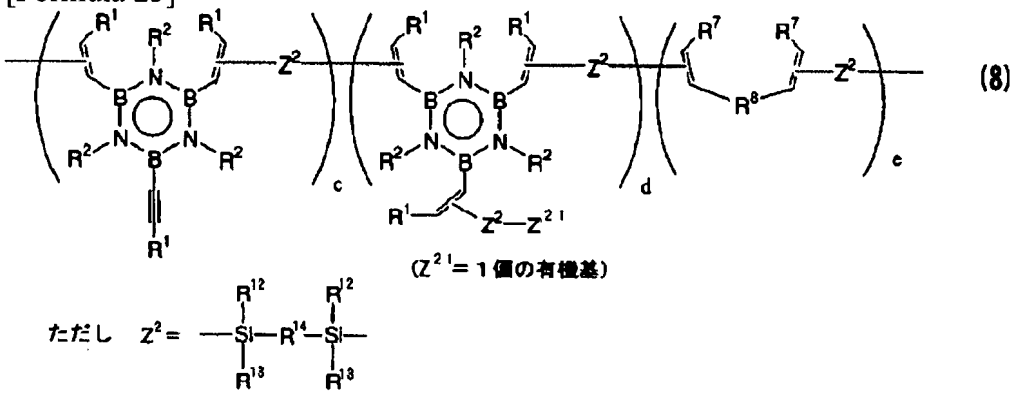
(1)

[0020] (-- a formula -- inside -- R -- one -- an alkyl group -- an aryl group -- an aralkyl -- a radical -- or -- a hydrogen atom -- being shown -- R -- two -- an alkyl group -- an aryl group -- an aralkyl -- a radical -- or -- a hydrogen atom -- being shown --) -- expressing -- having -- B -- B -- ' -- B -- " - a thoria -- RUKINIRU -- borazine -- a kind -- a general formula (6) --
(R7 C**C) mR8 (6)
Both the gene expressed with (R7 shows an alkyl group, an aryl group, an aralkyl radical, or a hydrogen atom among a formula, R8 shows a radical divalent [of the aromatic series which may have the substituent, or aliphatic series], or trivalent, and m is 3 in a radical trivalent in 2 and R8 with a radical divalent in R8), and the Tori Inn compound is used, and it is a general formula (7) about them.
[0021]
[Formula 22]



(7)

[0022] It is the borazine content silicon system copolymerization polymer which is made to react with the silicon compound which has at least two or more hydrosilyl radicals expressed with (the same or divalent radical of the aromatic series in which the univalent radical which is different from each other may be shown, and R14 may have the substituent as which R12 and R13 are chosen from an alkyl group, an aryl group, an aralkyl radical, or a hydrogen atom among a formula), and is obtained.
8. Following General Formula (8)
[0023]
[Formula 23]



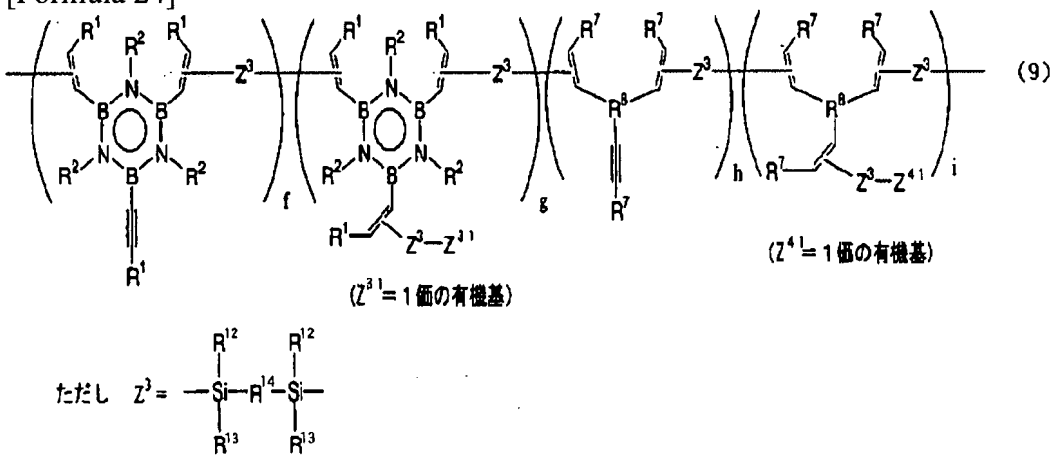
(8)

(Z²'= 1個の有機基)

ただし Z²=

[0024] Or a general formula (9)
[0025]

[Formula 24]



(9)

(Z^{31}= 1価の有機基) (Z^{41}= 1価の有機基)

ただし Z^3 =

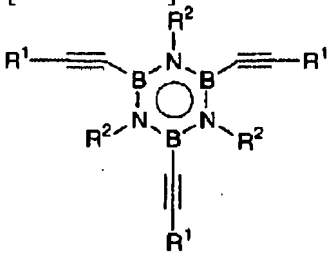
[0026] (R1, R2, R7, R8, R12, R13, and R14 among these formulas) It is the same as the thing in said general formula (1), (6), and (7), and c, d, e, f, g, h, and i are zero or more integers. a formula (8) -- c+d>=1, e>=1, and a formula (9) -- f+g>=1 and h+i>=1 -- it is -- a borazine content silicon system copolymerization polymer given in 7 characterized by having the repeat unit expressed.

9. 7 to which whenever [in the inside of air / 5% weight temperature decrease] is characterized by being 200 degrees C or more, or borazine content silicon system copolymerization polymer given in 8.

10. General formula (1)

[0027]

[Formula 25]



(1)

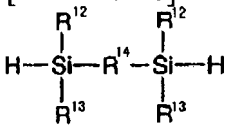
[0028] (-- a formula -- inside -- R -- one -- an alkyl group -- an aryl group -- an aralkyl -- a radical -- or -- a hydrogen atom -- being shown -- R -- two -- an alkyl group -- an aryl group -- an aralkyl -- a radical -- or -- a hydrogen atom -- being shown --) -- expressing -- having -- B -- B -- ' -- B -- " - a thoria -- RUKINIRU -- borazine -- a kind -- a general formula (6) --

(R7 C**C) mR8 (6)

Both the gene expressed with (R7 shows an alkyl group, an aryl group, an aralkyl radical, or a hydrogen atom among a formula, R8 shows a radical divalent [of the aromatic series which may have the substituent, or aliphatic series], or trivalent, and m is 3 in a radical trivalent in 2 and R8 with a radical divalent in R8), and the Tori Inn compound is used, and it is a general formula (7) about them.

[0029]

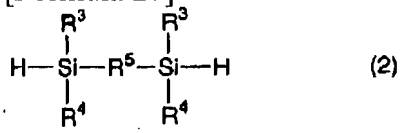
[Formula 26]



(7)

[0030] It is the manufacture approach of the thin film of the borazine content silicon system copolymerization polymer characterize by to mix with the silicon compound which has two hydrosilyl radicals express with (the same or divalent radical of the aromatic series in which the univalent radical which is different from each other may be show, and R14 may have the substituent as which R12 and

R13 are choose from an alkyl group, an aryl group, an aralkyl radical, or a hydrogen atom among a formula) under platinum catalyst existence, and to apply the solution.
[0031]
[Embodiment of the Invention] In said general formula (1), R2 shows an alkyl group, an aryl group, an aralkyl radical, or a hydrogen atom. the carbon number of an alkyl group -- 1-24 -- it is 1-12 preferably. the carbon number of an aryl group -- 6-20 -- it is 6-10 preferably. the carbon number of an aralkyl radical -- 7-24 -- it is 7-12 preferably. Instantiation of said R2 mentions aralkyl radicals, such as aryl groups, such as alkyl groups, such as a methyl group, an ethyl group, an isopropyl group, t-butyl, and an octyl radical, a phenyl group, a naphthyl group, and a biphenyl radical, benzyl, and a phenethyl radical, a hydrogen atom, etc.
[0032] these -- a substituent -- having -- a general formula -- (-- one --) -- expressing -- having -- B -- B -- ' -- B -- " - a thoria -- RUKINIRU -- borazine -- a compound -- an example -- ****** -- B, B', B"- TORIECHI nil borazine, B, B', B"- TORIECHINIRU-N, N', N"-trimethyl borazine, B, B', B"- Tori (1-propynyl) borazine, B, B', B"-Tori (phenyl ethynyl) borazine, B, B', B"- Tori (phenyl ethynyl)-N, N', N"-trimethyl borazine, Although B, B', B"- TORIECHINIRU-N, N', N"-triphenyl borazine, B, B', B"- Tori (phenyl ethynyl)-N, N', N"-triphenyl borazine, B, B', B"- ethynyl-N, N', N"-tribenzyl borazine, etc. are mentioned It is not limited to this. moreover -- one -- a kind -- B -- B -- ' -- B -- " - a thoria -- RUKINIRU -- borazine -- a compound -- independent -- it can also use -- although -- two -- a kind -- more than -- B -- B -- ' -- B -- " - a thoria -- RUKINIRU -- borazine -- a compound -- doubling -- using -- things -- this invention -- being advantageous -- voice -- it is contained like.
[0033] What the bis(hydrosilane) compound in the silicon compound which has two or more hydrosilyl radicals used by this invention is expressed with a general formula (2) to is mentioned.
[0034]
[Formula 27]

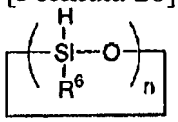


(2)

[0035] R3 and R4 show among a formula the identitas or the univalent radical which is different from each other chosen from an alkyl group, an aryl group, an aralkyl radical, or a hydrogen atom. the carbon number of an alkyl group -- 1-24 -- it is 1-12 preferably. the carbon number of an aryl group -- 6-20 -- it is 6-10 preferably. the carbon number of an aralkyl radical -- 7-24 -- it is 7-12 preferably. Instantiation of said R3 and R4 mentions aralkyl radicals, such as aryl groups, such as alkyl groups, such as a methyl group, an ethyl group, an isopropyl group, t-butyl, and an octyl radical, a phenyl group, a naphthyl group, and a biphenyl radical, benzyl, and a phenethyl radical, a hydrogen atom, etc.
[0036] Moreover, in said general formula (2), R5 shows the radical, the divalent oxygen atom, or divalent oxy-poly (dimethyl siloxy) radical of the aromatic series which may have the substituent. the carbon number of the divalent radical of aromatic series -- 6-24 -- it is 6-12 preferably. As a divalent radical of aromatic series, the arylene radical which contains hetero atoms, such as oxygen besides divalent aromatic hydrocarbon radicals (arylene radical etc.), as a connection radical is contained. Moreover, as a substituent which may be combined with the divalent radical of said aromatic series, an alkyl group, an aryl group, an aralkyl radical, etc. are contained. Instantiation of the case where R5 is the divalent radical of aromatic series mentions permutation arylene radicals, such as arylene radicals, such as a phenylene group, a naphthylene radical, and a biphenylene radical, and a diphenyl ether radical, etc.

[0037] It has these substituents and screws (mono-hydrosilane), screws (dihydrosilane), and screws (trihydro silane) are contained in the bis(hydrosilane) compound expressed with a general formula (2). As an example of these bis(hydrosilane) compound m-bis(dimethylsilyl) benzene, p-bis(dimethylsilyl) benzene, 1, 4-bis(dimethylsilyl) naphthalene, 1, 5-bis(dimethylsilyl) naphthalene, m-bis(methylethyl silyl) benzene, m-bis(methylphenyl silyl) benzene, A p-bis(methyl octyl silyl) benzene, 4, and 4'-bis

(methylbenzyl silyl) biphenyl, 4 and 4'-bis(methyl phenethyl silyl) diphenyl ether, m-bis(methyl silyl) benzene, Although m-disilyl benzene, 1, 1 and 3, 3-tetramethyl 1, 3-disiloxane, hydronalium dimethyl siloxy poly (dimethyl siloxy) dimethylsilane, etc. are mentioned, it is not limited to these.
[0038] Moreover, as a Pori (hydrosilane) compound in the silicon compound which has two or more hydrosilyl radicals, what is expressed with the following general formula (3) is mentioned, for example.
[0039]
[Formula 28]



(3)

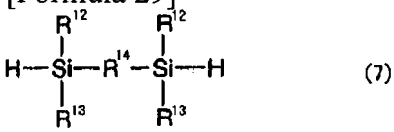
[0040] R6 shows an alkyl group, an aryl group, or an aralkyl radical among a formula, and n shows three or more integers. the carbon number of an alkyl group -- 1-24 -- it is 1-12 preferably. the carbon number of an aryl group -- 6-20 -- it is 6-10 preferably. the carbon number of an aralkyl radical -- 7-24 -- it is 7-12 preferably. Instantiation of said R6 mentions aralkyl radicals, such as aryl groups, such as alkyl groups, such as a methyl group, an ethyl group, an isopropyl group, t-butyl, and an octyl radical, a phenyl group, a naphthyl group, and a biphenyl radical, benzyl, and a phenethyl radical, etc. moreover, n -- three or more integers -- it is -- desirable -- 3-10 -- it is 3-6 more preferably.
[0041] Although 1, 3, 5, 7-tetramethyl cyclotetrasiloxane, 1, 3, 5 and 7, 9-pentamethyl cyclopentasiloxane, 1, 3 and 5, 7-tetraethyl cyclotetrasiloxane, 1 and 3, 5-triphenyl cyclotrisiloxane, 1, 3 and 5, 7-tetra-phenyl cyclotetrasiloxane, 1, 3 and 5, 7-tetra-benzyl cyclotetrasiloxane, etc. will be mentioned if these Pori (hydrosilane) compound is illustrated, it is not limited to these. Moreover, although one kind can also be independently used for the silicon compound which has two or more hydrosilyl radicals, it is contained in a mode with this invention advantageous [also using two or more kinds together].
[0042] this invention -- a general formula -- (-- one --) -- expressing -- having -- B -- B -- ' -- B -- " - a thoria -- RUKINIRU -- borazine -- a compound -- two -- a piece -- more than -- hydrosilyl -- a radical -- having -- silicon -- a compound -- reacting -- making -- a gene -- or -- Tori -- Inn -- a compound -- a general formula (6)
(R7 C**C) mR8 (6)
It is come out and expressed. R7 shows an alkyl group, an aryl group, an aralkyl radical, or a hydrogen atom among a formula. the carbon number of an alkyl group -- 1-24 -- it is 1-12 preferably. the carbon number of an aryl group -- 6-20 -- it is 6-14 preferably. the carbon number of an aralkyl radical -- 7-24 -- it is 7-16 preferably.
[0043] Instantiation of said R1 mentions aralkyl radicals, such as aryl groups, such as alkyl groups, such as a methyl group, an ethyl group, an isopropyl group, t-butyl, and an octyl radical, a phenyl group, a naphthyl group, and a biphenyl radical, benzyl, and a phenethyl radical, a hydrogen atom, etc. Moreover, R8 shows a radical divalent [of the aromatic series which may have the substituent, or aliphatic series], or trivalent. m is 3 in a radical trivalent in 2 and R8 with a radical divalent in R8. the carbon number of a radical divalent [of aromatic series], or trivalent -- 6-20 -- it is 6-14 preferably. moreover, the carbon number of a radical divalent [of aliphatic series], or trivalent -- 2-20 -- it is 3-16 preferably.
Instantiation of said R8 mentions a phenylene group, a benzene Trier radical, a naphthylene radical, a naphthalene Trier radical, anthrylene group, a biphenylene radical, the Tell phenylene group, ethylene, a trimethylene radical, a pentamethylene radical, an octamethylene radical, a dodeca methylene group, a hexadecamethylene radical, etc.
[0044] When these genes or the Tori Inn compound is illustrated, p- and m-diethynyl benzene, 1, 3, and 5- and 1 and 2, 4-TORIECHI nil benzene, p-, and m-JI (1-propynyl) benzene, 1, 3, and 5- and 1 and 2, 4-Tori (1-propynyl) benzene, p- and m-JI (phenyl ethynyl) benzene, p-, and m-JI (3-phenyl-1-propynyl) benzene, 1, 3, and 5- and 1 and 2, 4-Tori (phenyl ethynyl) benzene, 1 and 4- and 1, 5-diethynyl naphthalene, 9, a 10-diethynyl anthracene, Although a 4 and 4'-diethynyl biphenyl, 1, 5-hexadiyne, 1, 6-hepta-gene, 1, 8-nonadiyne, 1, and 11-dodeca gene, 1, 15-hexa deca gene, 1, 19-eicosa gene, etc. are

mentioned, it is not limited to these. Although one kind can also be independently used for a gene or the Tori Inn compound, it is contained in a mode with this invention advantageous [also using two or more kinds together].

[0045] As a silicon compound which has two or more hydrosilyl radicals used by this invention, what is expressed with a general formula (7) is used.

[0046]

[Formula 29]



(7)

[0047] R12 and R13 show among a formula the identitas or the univalent radical which is different from each other chosen from an alkyl group, an aryl group, an aralkyl radical, or a hydrogen atom. the carbon number of an alkyl group -- 1-24 -- it is 1-12 preferably. the carbon number of an aryl group -- 6-20 -- it is 6-10 preferably. the carbon number of an aralkyl radical -- 7-24 -- it is 7-12 preferably. Instantiation of said R12 and R13 mentions aralkyl radicals, such as aryl groups, such as alkyl groups, such as a methyl group, an ethyl group, an isopropyl group, t-butyl, and an octyl radical, a phenyl group, a naphthyl group, and a biphenyl radical, benzyl, and a phenethyl radical, a hydrogen atom, etc.

[0048] Moreover, in said general formula (7), R14 shows the divalent radical of the aromatic series which may have the substituent. the carbon number of the divalent radical of aromatic series -- 6-24 -- it is 6-12 preferably. As a divalent radical of aromatic series, the arylene radical which contains hetero atoms, such as oxygen besides divalent aromatic hydrocarbon radicals (arylene radical etc.), as a connection radical is contained. Moreover, as a substituent which may be combined with the divalent radical of said aromatic series, an alkyl group, an aryl group, an aralkyl radical, etc. are contained. As a divalent radical of such aromatic series, permutation arylene radicals, such as arylene radicals, such as a phenylene group, a naphthylene radical, and a biphenylene radical, and a diphenyl ether radical, etc. are mentioned, for example.

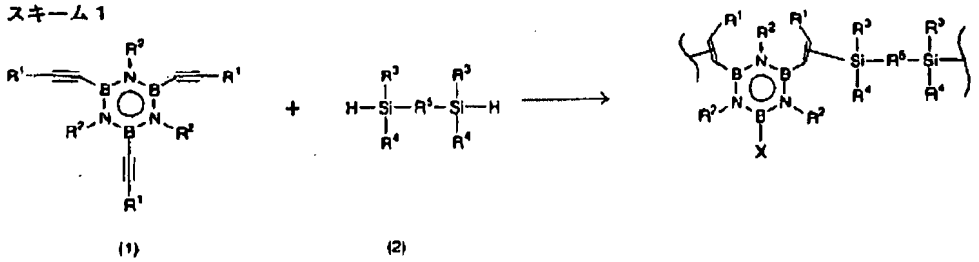
[0049] It has these substituents and screws (mono-hydrosilane), screws (dihydrosilane), and screws (trihydro silane) are contained in the bis(hydrosilane) compound expressed with a general formula (7). As an example of these bis(hydrosilane) compound m-bis(dimethylsilyl) benzene, p-bis(dimethylsilyl) benzene, 1, 4-bis(dimethylsilyl) naphthalene, 1, 5-bis(dimethylsilyl) naphthalene, m-bis(methylethyl silyl) benzene, m-bis(methylphenyl silyl) benzene, Although - bis(methylbenzyl silyl) biphenyl, and p-bis(methyl octyl silyl) benzene, 4, and 4 '4, 4'-bis(methyl phenethyl silyl) diphenyl ether, m-bis(methyl silyl) benzene, m-disilyl benzene, etc. are mentioned It is not limited to these.

[0050] The reaction of the compound expressed with the general formula (1) of this invention and the silicon compound which has at least two or more hydrosilyl radicals expressed with a general formula (2) or (3) is shown by the following schemes 1 and 2.

[0051]

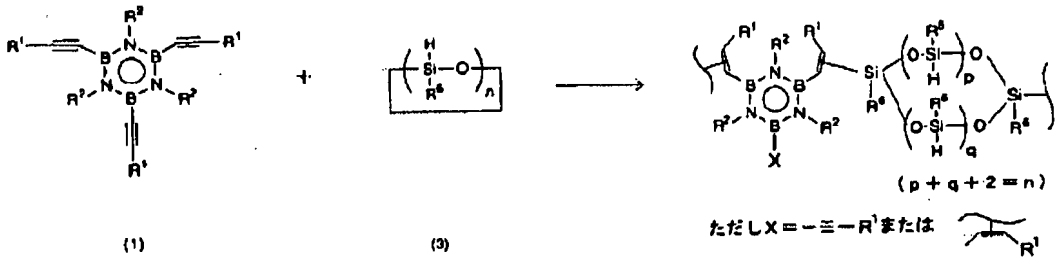
[Formula 30]

スキーム 1



(1) (2)

スキーム 2



(1) (3)

[0052] The mole ratio of a silicon compound which has B, B', and at least two hydrosilyl radicals to a B"-thoria RUKINIRU borazine compound is carried out in 0.1-10, and the range of the amount relation of the raw material compound in the above-mentioned reaction is 0.2-5 preferably.

[0053] What is conventionally used for hydrosilylation can be used for the platinum content catalyst used by this invention. Although platinum divinyl tetramethyl disiloxane, a platinum annular divinyl methyl siloxane, chloroplatinic acid, dichloro platinum, platinum carbon, tris (JIBEN zylidene acetone) 2 platinum, bis(ethylene) tetra-chloro 2 platinum, cyclo-octadiene dichloro platinum, bis(cyclo-octadiene) platinum, cyclo-octadiene dimethyl platinum, bis(triphenyl phosphine) dichloro platinum, tetrakis (triphenyl phosphine) platinum, etc. will be mentioned if this is illustrated, it is not limited to this.

[0054] These platinum content catalyst is used in 0.000001-0.5 by the mole ratio of a B, B', and metal [as opposed to a raw material with little molar quantity among a B"-thoria RUKINIRU borazine compound or bis(hydrosilane) compounds] atom.

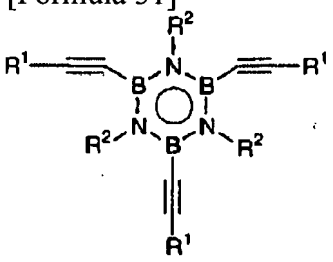
[0055] Although it can carry out irrespective of the existence of a solvent, when using a solvent, a raw material and the various solvents except what reacts can be used for this invention. As these solvents, solvents, such as an aromatic hydrocarbon system, a saturated hydrocarbon system, an aliphatic series ether system, and an aromatic series ether system, are mentioned, and, more specifically, toluene, benzene, a xylene, a hexane, a tetrahydrofuran, diphenyl ether, etc. are mentioned.

[0056] Moreover, in case the thin film of the borazine content silicon polymer of this invention is formed, there is especially no limit and, as for the method of application of the solution to a base material top, spreading with the brush, a spray coating cloth, spreading by the spin coat method, etc. can also take which approach. As temperature which prepares the solution applied by this invention, although a room temperature is generally sufficient, since a desirable rate is attained, it can also cool or heat in -20 to 200 degrees C according to the structure of a source material. As desirable temperature, 150 degrees C is more preferably carried out in 0 to 100 degrees C from 0 degree C.

[0057] After applying a solution, the thin film of a borazine content silicon system polymer can be obtained by making it dry in air, under an inert atmosphere, or in a vacuum. Especially the thin film of a borazine content silicon system polymer means not the semantics that restricts the thickness but not which massive resin but the thing formed in the shape of film here. Especially according to this invention approach, it is the description that the film can be formed in the range from the thin film of mum unit to the film of comparatively thick mm order, and there is especially no upper limit of membranous thickness.

[0058] Moreover, according to this invention, it is a general formula (1).

[Formula 31]

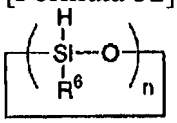


(1)

[0059] (-- a formula -- inside -- R -- one -- an alkyl group -- an aryl group -- an aralkyl -- a radical -- or -- a hydrogen atom -- being shown -- R -- two -- an alkyl group -- an aryl group -- an aralkyl -- a radical -- or -- a hydrogen atom -- being shown --) -- expressing -- having -- B -- B -- ' -- B -- " - a thoria -- RUKINIRU -- borazine -- a compound -- a general formula (3) --

[0060]

[Formula 32]

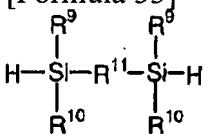


(3)

[0061] (R6 shows an alkyl group, an aryl group, or an aralkyl radical among a formula, and n shows three or more integers) Or a general formula (4)

[0062]

[Formula 33]

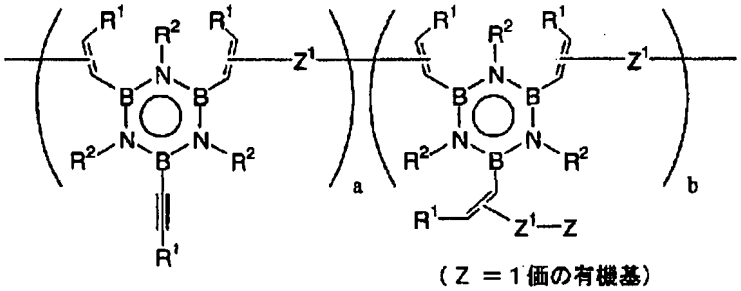


(4)

[0063] (-- R9 and R10 are chosen from an alkyl group, an aryl group, an aralkyl radical, or a hydrogen atom among a formula -- the same -- or -- difference -- a univalent radical is shown and R11 shows an oxy-poly (dimethyl siloxy) radical --) -- making the silicon compound which has at least two or more hydrosilyl radicals expressed react -- a general formula (5)

[0064]

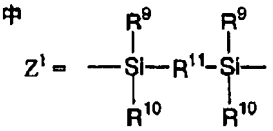
[Formula 34]



(5)

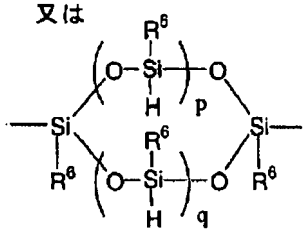
(Z ＝1価の有機基)

式中



(化合物（4）との反応の場合)

又は



(化合物（3）との反応の場合)

(p + q + 2 = n)

を示す。

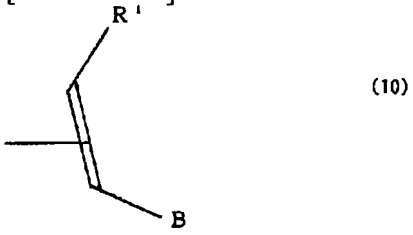
[0065] (-- R1, R2, R9, R10, R11, and R6 are the same as the thing in said general formula (1), (3), and (4) among a formula, and a and b are a+b>=1 for zero or more integers --) -- the new borazine content silicon system polymer which has the structure expressed is offered.

[0066] As an example of R1, R2, and R5, what was shown by previous explanation can be mentioned among these formulas. Moreover, as an example of R9 and R10, what was shown by explanation of the point of R3 and R4 is mentioned. R11 is an oxy-poly (dimethyl siloxy) radical. on the other hand -- a and b -- zero or more integers -- it is -- a+b -- one or more -- it is -- desirable -- 1-50000 -- it is the integer of 1-20000 more preferably. Moreover, Z is a univalent organic radical originating in a raw material compound, for example, is a vinyl group, a hydrogen atom, etc. which may have the substituent. The radical of the end in these polymers is a hydrosilyl radical or an ethynyl group.

[0067] Moreover, the part expressed with the following formula (10) in said general formula (5) means that four kinds of integrated states shown in the following formula (11) are included.

[0068]

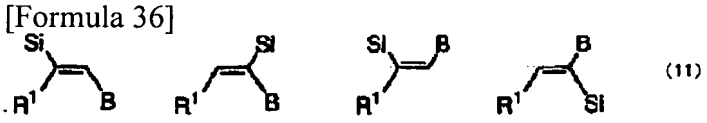
[Formula 35]



(10)

[0069]

[Formula 36]



(11)

[0070] In manufacture of the polymer of this invention, since a reaction advances almost quantitatively,

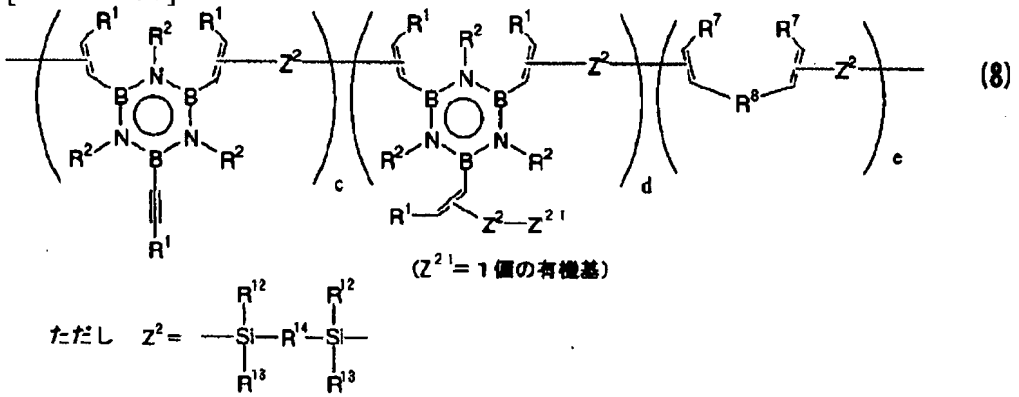
the purpose polymer is easily obtained by the approach of removing a solvent under reduced pressure or ordinary pressure. Moreover, it can also isolate preparatively by approaches, such as reprecipitation and gel permeation chromatography.

[0071] this invention -- a claim -- seven -- or -- ten -- indicating -- having had -- invention -- it can set -- a raw material -- a compound -- an amount -- relation -- a general formula -- (-- one --) -- B -- B -- ' -- B -- " - a thoria -- RUKINIRU -- borazine -- a compound -- receiving -- the gene or the Tori Inn compound of a general formula (6) of arbitration -- it can be used -- although -- general -- the mole ratio -- 0.01-200 -- desirable -- 0.03-150 -- it is the range of 0.05-100 more preferably. [of a mole ratio] B, B', and B" -- the ratio of the molar quantity of a silicon compound which has two hydrosilyl radicals of a general formula (7) to the molar quantity which set - thoria RUKINIRU borazine compound (1), the gene, or the Tori Inn compound (6) -- general -- 0.1-10 -- it is the range of 0.2-5 preferably.

[0072] It is the following general formula (8) by making these monomers usually react to the bottom of existence of a platinum content catalyst in this invention.

[0073]

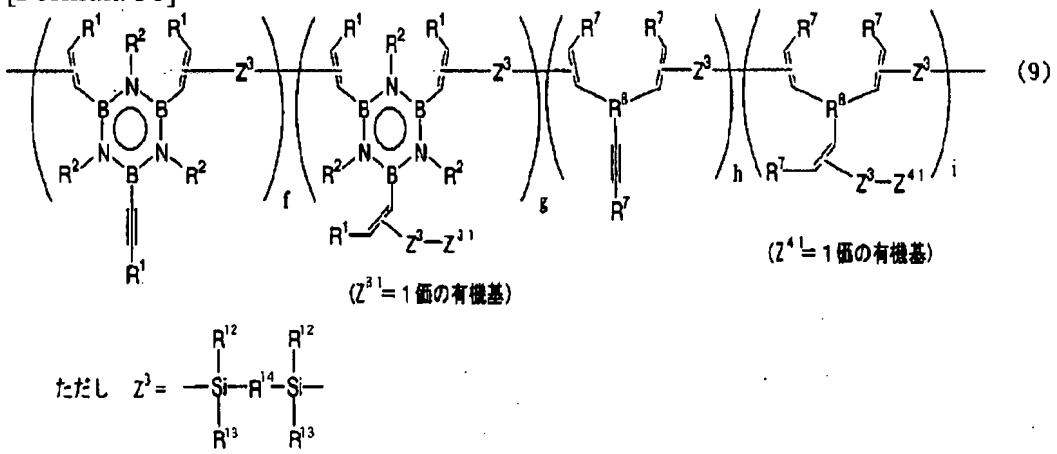
[Formula 37]



[0074] Or a general formula (9)

[0075]

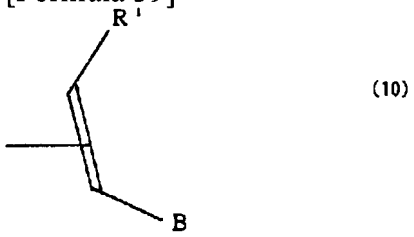
[Formula 38]



[0076] (R1, R2, R7, R8, R12, R13, and R14 among these formulas) It is the same as the thing in said general formula (1), (6), and (7), and c, d, e, f, g, h, and i are zero or more integers. a formula (8) -- c+d>=1, e>=1, and a formula (9) -- f+g>=1 and h+i>=1 -- it is -- the borazine content silicon system copolymerization polymer of the new 3 yuan system which has the repeat unit expressed can be obtained. Among a formula, Z21, Z31, and Z41 are the univalent organic radicals originating in a raw material compound, for example, are a vinyl group, a hydrogen atom, etc. which may have the substituent. The radical of the end in these polymers is a hydrosilyl radical or an ethynyl group.

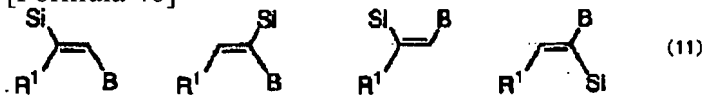
[0077] Moreover, the part expressed with said general formula (8) or the following formula (10) in (9)

means that four kinds of integrated states shown in the following formula (11) are included.
[0078]
[Formula 39]



(10)

[0079]
[Formula 40]



(11)

[0080] In the above-mentioned reaction, although the platinum catalyst shown previously is used, these platinum content catalyst is used in 0.000001-0.5 by the mole ratio of a B, B', and metal [as opposed to a raw material with little molar quantity among the total quantity of B"-thoria RUKINIRU borazine compound (1), a gene, or the Tori Inn compound (6), or bis(hydrosilane) compounds (7)] atom. In manufacture of the above-mentioned polymer, since a reaction advances almost quantitatively, the purpose polymer is easily obtained by the approach of removing a solvent under reduced pressure or ordinary pressure. Moreover, it can also isolate preparatively by approaches, such as reprecipitation and gel permeation chromatography.
[0081] Although it can carry out irrespective of the existence of a solvent, a reaction can use a raw material and the various solvents except what reacts, when using a solvent. As these solvents, solvents, such as an aromatic hydrocarbon system, a saturated hydrocarbon system, an aliphatic series ether system, and an aromatic series ether system, are mentioned, and, more specifically, toluene, benzene, a xylene, a hexane, a tetrahydrofuran, diphenyl ether, etc. are mentioned.
[0082] In this invention, the thin film of the borazine content silicon system copolymerization polymer which was [thermal resistance / flammability-proof,] excellent can be obtained by reacting to the bottom of existence of these solvents and a platinum content catalyst, and applying the solution obtained to a base material etc. In case the thin film of the borazine content silicon system copolymerization polymer of this invention is formed, there is especially no limit and, as for the method of application of the solution to a base material top, spreading with the brush, a spray coating cloth, spreading by the spin coat method, etc. can also take which approach. As temperature which prepares the solution applied by this invention, although a room temperature is generally sufficient, since a desirable rate is attained, it can also cool or heat in -20 to 200 degrees C according to the structure of a source material. As desirable temperature, 150 degrees C is more preferably carried out in 0 to 100 degrees C from 0 degree C.
[0083] After applying a solution, the thin film of a borazine content silicon system copolymerization polymer can be obtained by making it dry in air, under an inert atmosphere, or in a vacuum. In this invention, especially the thin film of a borazine content silicon system copolymerization polymer means not the semantics that restricts the thickness but not which massive resin but the thing formed in the shape of film. Especially according to this invention approach, it is the description that the film can be formed in the range from the thin film of mum unit to the film of comparatively thick mm order, and there is especially no upper limit of membranous thickness.
[0084]
[Example] Next, although an example explains this invention to a detail further, this invention is not limited to these examples.
[0085] (Example 1) B, B', B"- TORIECHINIRU-N, N', N"-trimethyl borazine (0.25mmol), and p-bis (dimethylsilyl) benzene (0.25mmol) were dissolved in toluene (5ml), 2% xylene solution (0.00025mmol

platinum) of platinum of platinum divinyl tetramethyl disiloxane was added, and it agitated for four days at the room temperature under nitrogen. The transparent and colorless thin film was obtained by applying 0.1ml of this solution on a glass substrate, and making it dry in air. The thickness of the thin film measured using TARISU tetraethylpyrophosphate was 2 micrometers. This thin film was thermal resistance, and as a result of measuring the thermal stability of the polymer of this film by thermogravimetric analysis, whenever [5% weight temperature decrease] were 490 degrees C (under nitrogen), and 430 degrees C (inside of air).
1 H-NMR (C6D6, delta, ppm) 7.9-7.4 (m, 4H), 7.2-6.9 (m, 0.5H) and 6.9-6.7 (m, 0.5H), 6.6-6.4 (m, 0.5H) and 6.2-5.6 (m, 2.5H), 3.5-2.5 (m, 10H), 0.6-0.2(br s, 12H).IR (KBr disk, cm-1) 2072, and 1580 (w), 1500-1350 (peak top, 1448, 1396), 1247, 1133, and 1085 (w) and 1004 (w), (w) and 648 (w). elemental-analysis C19H30N3B3Si2: A theoretical value C and 58.66; H, 7.77; N, 10.80. Actual measurement C, 57.50; H, 7.82; 951, 841, 772 N, 9.83. [0086] (Example 2) B, B', B"- TORIECHINIRU-N, N', N"-trimethyl borazine (0.25mmol), 1, 3 and 5, and 7-tetramethyl cyclotetrasiloxane (0.25mmol) were dissolved in toluene (5ml), 2% xylene solution (0.00025mmol platinum) of platinum of platinum divinyl tetramethyl disiloxane was added, and it agitated for two days at the bottom room temperature of nitrogen. The transparent and colorless thin film was obtained by applying 0.1ml of this solution on a glass substrate, and making it dry in air. The thickness of the thin film measured using TARISU tetraethylpyrophosphate was 4 micrometers. This thin film showed the thermal resistance which was excellent like the example 1.
IR KBr disk, cm-1 2164, 1230, 1021, 909, 731. [0087] B, B', B"- TORIECHINIRU-N, N', N"-trimethyl borazine (0.25mmol), (Example 3) hydronalium dimethyl siloxy poly (dimethyl siloxy) dimethylsilane (HMe2SiO(SiMe2O) rSiMe2H --) Mn=6000;0.25mmol was dissolved in toluene (0.5ml), 2% xylene solution (0.00025mmol platinum) of platinum of platinum divinyl tetramethyl disiloxane was added, and under nitrogen, as a result of agitating at a room temperature for 1 hour, the gel solution was obtained. Under reduced pressure of a reaction solution, heating concentration was carried out and the powder-like borazine content silicon system polymer (5a) was obtained with almost quantitive yield.
[0088] IR KBr disk, cm-1 2056, 1945, 1593, 1470-1350, 1320-1220, 1200-900. elemental analysis C201H486N3O81B3Si81: A theoretical value C and 33.12; H, 8.09. Actual measurement C, 32.91;H, 8.24. thermogravimetric analysis (inside of nitrogen)
Td5 (whenever [5% weight temperature decrease]) 329-degree-C26% ** (985 degrees C)
Thermogravimetric analysis (inside of air)
Td5 (whenever [5% weight temperature decrease]) 333-degree-C36% ** (985 degrees C)
[0089] (Example 4) B"- TORIECHINIRU-N, N', N"-trimethyl borazine (0.25mmol), 1, 3 and 5, and 7-tetramethyl cyclotetrasiloxane (0.25mmol) were dissolved in toluene (0.5ml), 2% xylene solution (0.00025mmol platinum) of platinum of platinum divinyl tetramethyl disiloxane was added, and under nitrogen, B, B', and as a result of agitating at a room temperature for 2 hours, the gel solution was obtained. Under reduced pressure of a reaction solution, heating concentration was carried out and the powder-like borazine content silicon system polymer (5b) was obtained with almost quantitive yield. This polymer has the same structure as the polymer of an example 2.
[0090] Thermogravimetric analysis (inside of nitrogen)
Td5 (whenever [5% weight temperature decrease]) 204-degree-C81% ** (985 degrees C)
Thermogravimetric analysis (inside of air)
Td5 (whenever [5% weight temperature decrease]) 200-degree-C83% ** (985 degrees C)
[0091] (Example 5) B, B', B"- TORIECHINIRU-N, N', N"-trimethyl borazine (0.125mmol), m-diethynyl benzene (0.125mmol), and p-bis(dimethylsilyl) benzene (0.25mmol) were dissolved in toluene (5ml), 2% xylene solution (0.00025mmol platinum) of platinum of platinum divinyl tetramethyl disiloxane was added, and it agitated for four days at the bottom room temperature of nitrogen. The transparent and colorless thin film was obtained by applying 0.1ml of this solution on a glass substrate, and making it dry in air. The thickness of the thin film measured using TARISU tetraethylpyrophosphate was 2 micrometers. As a result of measuring the thermal stability of the polymer of this film by thermogravimetric analysis, whenever [5% weight temperature decrease] were

320 degrees C (under nitrogen), and 360 degrees C (inside of air).
1 H-NMR (C6D6, delta, ppm) 8.1-7.9 (m, 0.7H), 7.8-7.6 (m, 3.4H) and 7.5-7.1 (m, 0.7H), 6.9-6.7 (m, 0.9H) and 6.6-6.4 (m, 0.8H), 6.2-5.7 (m, 1.5H), 3.5-2.5 (m, 5H), and 0.6-0.2.(br s, 12H) IR (KBr disk, cm-1) 2072 (w), 1578, 1446, 1396, 1249, 1133, 1104, 1019, 839, 774. [0092] (Example 6) B, B', B"-TORIECHINIRU-N, N', N"-trimethyl borazine (0.125mmol), 1 and 3, 5-TORIECHI nil benzene (0.125mmol), and p-bis(dimethylsilyl) benzene (0.25mmol) were dissolved in toluene (5ml), 2% xylene solution (0.00025mmol platinum) of platinum of platinum divinyl tetramethyl disiloxane was added, and it agitated for four days at the bottom room temperature of nitrogen. The transparent and colorless thin film was obtained by applying 0.1ml of this solution on a glass substrate, and making it dry in air. The thickness of the thin film measured using TARISU tetraethylpyrophosphate was 3 micrometers. As a result of measuring the thermal stability of the polymer of this film by thermogravimetric analysis, whenever [5% weight temperature decrease] were 320 degrees C (under nitrogen), and 380 degrees C (inside of air).
IR KBr disk, cm-1 2120, 2074, 1578, 1448, 1381, 1251, 1135, 988, 880,820. [0093] (Example 7) B"-TORIECHINIRU-N, N', N"-trimethyl borazine (0.125mmol), m-diethynyl benzene (0.125mmol), and p-bis(dimethylsilyl) benzene (0.25mmol) were dissolved in toluene (0.5ml), 2% xylene solution (0.00025mmol platinum) of platinum of platinum divinyl tetramethyl disiloxane was added, and under nitrogen, B, B', and as a result of agitating for five days at a room temperature, the gel solution was obtained. Under reduced pressure of a reaction solution, heating concentration was carried out and the powder-like borazine content silicon system copolymerization polymer (4a) was obtained with almost quantitive yield. This polymer has the same structure as the polymer of an example 1.
Thermogravimetric analysis (inside of nitrogen)
Td5 (whenever [5% weight temperature decrease]) 321-degree-C63% ** (985 degrees C)
Thermogravimetric analysis (inside of air)
Td5 (whenever [5% weight temperature decrease]) 362-degree-C59% ** (985 degrees C)
[0094] B, B', B"- TORIECHINIRU-N, N', N"-trimethyl borazine (0.125mmol), (Example 8) 1, 3, 5-TORIECHI nil benzene (0.125mmol), and p-bis(dimethylsilyl) benzene (0.25mmol) It dissolved in toluene (0.5ml) and 2% xylene solution (0.00025mmol platinum) of platinum of platinum divinyl tetramethyl disiloxane was added, and under nitrogen, as a result of agitating for six days at a room temperature, the gel solution was obtained. Under reduced pressure of a reaction solution, heating concentration was carried out and the powder-like borazine content silicon system copolymerization polymer (5a) was obtained with almost quantitive yield. This polymer has the same structure as the polymer of an example 2.
Thermogravimetric analysis (inside of nitrogen)
Td5 (whenever [5% weight temperature decrease]) 322-degree-C75% ** (985 degrees C)
Thermogravimetric analysis (inside of air)
Td5 (whenever [5% weight temperature decrease]) 382-degree-C66% ** (985 degrees C)
[0095]
[Effect of the Invention] While being able to manufacture the thin film of a borazine content silicon system polymer which functions as flammability-proof, heat-resistant coating film, etc. to simple and insurance from B, B', and a B"-thoria RUKINIRU borazine compound and the silicon compound which has at least two hydrosilyl radicals according to this invention, an available new borazine content silicon system polymer can also be obtained industrially. Moreover, by making it react with B, B', and the silicon compound (3) that has at least two hydrosilyl radicals for B"-thoria RUKINIRU borazine compound (1) and the usual gene, or the Tori Inn compound (2) The thin film excellent in the flammability-proof of the borazine content silicon system copolymerization polymer of the new 3 yuan system which stopped the amount of the expensive borazine monomer used, and this copolymerization polymer, and thermal resistance can be manufactured to simple and insurance. Therefore, the industrial meaning of this invention is great.